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- (54) [Title of the Invention] WATER PIPE HAVING COATED INNER SURFACE AND PRODUCTION METHOD THEREFOR

(57) [Abstract]

[Object] To provide a water pipe capable of preventing environmental hormones from entering tap water while maintaining the good adhesion to the inner surface of the water pipe and corrosion resistance of a coating film.

[Means for Solving the Problem] A water pipe having a coated inner surface, comprising a water pipe unit, an epoxy resin coating layer formed on the inner surface of the water pipe unit, and an acrylic resin coating layer or polyester resin coating layer formed on the surface of the epoxy resin coating layer; and a method for producing a water pipe having a coated inner surface, the method comprising the steps of applying an epoxy resin powder coating composition to the inner surface of a water pipe, and applying an acrylic resin powder coating composition or polyester resin powder coating composition to the epoxy resin powder coating layer.

[Claims]

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[Claim 1] A water pipe having a coated inner surface, comprising a water pipe unit, an epoxy resin coating layer formed on the inner surface of the water pipe unit, and an acrylic resin coating layer or polyester resin coating layer formed on the surface of the epoxy resin coating layer.

[Claim 2] A method for producing a water pipe having a coated inner surface, the method comprising the steps of applying an epoxy resin powder coating composition to the inner surface of a water pipe, and applying an acrylic resin powder coating composition or polyester resin powder coating composition to the epoxy resin powder coating layer.

[0001] [Detailed Description of the Invention]

[Field of Industrial Application] The present invention relates to an inner-surface-coated water pipe and a production method therefor. In particular, the present invention relates to an inner-surface-coated water pipe for use in providing safe tap water, the inner surface of which is coated to have two coating layers, with the overcoat layer being composed of a coating layer that has no risk of contaminating tap water; and a production method therefor.

[0002]

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[Prior Art] Cast-iron pipes and electric-resistance-welded pipes have been used as water pipes. The inner surfaces of such pipes easily rust and are thus furnished with a coating composition as an anticorrosive. Epoxy resin coating compositions have been used in the form of solventless coating compositions or powder coating compositions as such coating compositions due to their good adhesion to the substrate and corrosion resistance.

- [0003] However, when epoxy resin coating compositions are coated and then cured, unpolymerized bisphenol A remains in the coating layer; bisphenol A is an environmental hormone. Therefore, epoxy resin coating compositions have recently been considered problematic in that they
- adversely affect the human body because unpolymerized bisphenol A leaches out into tap water.

[0004]

[Problems to Be Solved by the Invention] However, since among a variety of coating compositions epoxy resin

20 coating compositions have excellent adhesion to the inner surface of water pipes, superior corrosion resistance, and like characteristics, it is currently not very beneficial to use other coating compositions for application to the inner surface of water pipes.

25 [0005] The present invention provides a water pipe that

can prevent environmental hormones from entering tap water while maintaining the good adhesion and corrosion resistance by applying as an undercoat an epoxy resin coating composition to the inner surface of a water pipe and applying as an overcoat an acrylic resin coating composition or polyester resin coating composition; and a production method therefor.

[0006]

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[Means for Solving the Problems] The inventors found that the problem of environmental hormones entering tap water 10 can be solved while maintaining the good adhesion and corrosion resistance by creating on the inner surface of a water pipe a two-layer structure composed of an undercoat layer to give corrosion resistance to the water pipe and an overcoat layer to prevent hazardous substances 15 contained in the undercoat layer from entering tap water, and thereby accomplished the present invention. [0007] The inner-surface-coated water pipe of the invention comprises a water pipe unit, an epoxy resin coating layer formed on the inner surface of the water 20 pipe unit, and an acrylic resin coating layer or polyester resin coating layer formed on the surface of the epoxy resin coating layer. The method for producing an innersurface-coated water pipe of the invention comprises the steps of applying an epoxy resin powder coating 25

composition to the inner surface of a water pipe, and applying an acrylic resin powder coating composition or polyester resin powder coating composition to the epoxy resin powder coating layer.

5 [0008]

[Mode for Carrying Out the Invention] The present invention is described below in detail. In the present invention, any conventional solid resin of bisphenol Atype having a softening temperature of at least 60°C and an epoxy equivalent of at least 500 can be used as the 10 resin component of the coating composition for forming the epoxy resin coating layer, i.e., the undercoat layer, and may be partially modified by replacement with a novolactype epoxy resin, cresol novolac-type epoxy resin, phenol 15 novolac-type epoxy resin, alkylphenol novolac-type epoxy resin, etc. Such epoxy resins can be used singly or in combination. Moreover, such epoxy resins can be used in combination with polyester resins and acrylic resins that have a carboxyl group within the resin molecule. Blocked isocyanate resins, polyfunctional carboxylic acids, 20 polyfunctional acid anhydrides, dicyandiamine, imidazoles, etc., can be used concomitantly as curing agents. [0009] In addition to such resins and curing agents, it is effective to use coloring pigments and antirust pigments 25 as coating film components to enhance the strength,

corrosion resistance, and the like of the film; additives to impart other characteristics; etc. Examples of coloring pigments include yellow iron oxide, titanium yellow, red iron oxide, titanium oxide, like inorganic pigments; permanent yellow FGL, phthalocyanine blue, indanthrene blue RS, permanent red F5RK, brilliant first scarlet G, and like organic pigments; etc. The amount of coloring pigment in the resin particles is usually about 0.5% to about 60% in PWC. Coloring pigments need not be used in the case of clear coating compositions.

[0010] PWC herein refers to pigment weight concentration and can be calculated using the following equation:

PWC = [(Contained pigment in weight percent) / (Total solids content of coating composition in weight percent)]

15 x 100

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When the amount of pigment is excessive, and especially when the amount of pigment with high oil absorbency is excessive, the resulting coating film formed from such a coating composition is likely to have an impaired

20 smoothness.

[0011] Moreover, barium sulfate, barium carbonate, calcium carbonate, clay, silica powder, silicic acid fine powder, diatomaceous earth, talc, basic magnesium carbonate, alumina white, etc., can be added as extender pigments to control the gloss level and hardness of the coating film.

[0012] Flaky pigments may be added to enhance the strength and corrosion resistance of the coating film. Aluminium pigments, mica pigments, metal powders, flaky glass powders, plastic film pieces, etc., can be used as flaky pigments. Such pigments can be used singly or as a combination of two or more kinds. In particular, adding glass flakes, mica pigments, or metal powdery pigments as fine flaky pigments is more effective in enhancing corrosion resistance than adding extender pigments although the material costs of the coating composition are 10 likely to be increased accordingly. [0013] In the present invention, the overcoat layer is formed to prevent leaching of hazardous substances from the undercoat epoxy resin coating layer. Thus, it is necessary to form, as the overcoat layer, a coating film 15 containing no hazardous substances at all. Accordingly, in the present invention, an acrylic resin coating composition or polyester resin coating composition is used to form an overcoat layer for coating the inner surface of 20 water pipes. In the production of the acrylic resin for use in the overcoat layer, materials that are suspected of being environmental hormones, such as styrene monomers, cannot be used. For the same reason, triphenyl tin, tributyl tin and the like cannot be used as a

polymerization catalyst in production of the polyester

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methacrylate, stearyl methacrylate, cyclohexyl methacrylate, propyl methacrylate, benzyl methacrylate, isopropyl methacrylate, sec-butyl methacrylate, 2hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, allyl methacrylate, ethylene glycol methacrylate, triethylene glycol methacrylate, tetraethylene glycol methacrylate, 1,3-butylene glycol 10 methacrylate, trimethylolpropane methacrylate, 2ethoxyethyl methacrylate, 2-methoxyethyl methacrylate, dimethylaminoethyl methyl chloride salt methacrylate, methacrylic acid, sodium methacrylate and like methacrylic acid and methacrylic ester monomers. In addition to such acrylic monomers, acrylamide, acrylonitrile, vinyl acetate, 15 ethylene, propylene, isobutylene, butadiene, isoprene, chloroprene and like vinyl monomers can be used as copolymerization components.

[0015] Other usable copolymerization components include
20 epoxy-containing ethylenically unsaturated monomers,
carboxy-containing ethylenically unsaturated monomers,
hydroxy-containing ethylenically unsaturated monomers, etc.
Examples of epoxy-containing ethylenically unsaturated
monomers include glycidyl (meth)acrylate, methylglycidyl

25 (meth)acrylate, allylglycidyl ether, 3,4-

-10epoxycyclohexylmethyl (meth)acrylate, etc. Examples of carboxyl-containing ethylenically unsaturated monomers include (meth) acrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, etc. Examples of hydroxycontaining ethylenically unsaturated monomers include hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, etc. [0016] The polymerization for producing the acrylic acid for use in the present invention can be carried out by a 10 process in which, after synthesizing a high-molecularweight resin by a conventional solution polymerization procedure, the solvent is removed and collected by thinfilm heating-decompression or like method to prepare a solid resin; or by a process in which, after synthesizing 15 a resin by a suspension polymerization procedure, the moisture is removed by spray-drying or like method to prepare a solid resin. [0017] When the reactive polar group in the acrylic resin is a glycidyl group, a multifunctional carboxy-containing 20 compound such as sebacic acid, dodecanedicarboxylic acid, etc., a multifunctional acid anhydride or the like can be used as a curing agent for the acrylic resin. When the reactive polar group in the acrylic resin is a hydroxy group or a combination of a hydroxy group and a carboxy group, a blocked isocyanate resin, melamine resin or the 25

thereof; malic acid, tartaric acid, 1,2-hydroxystearic acid, paraoxybenzoic acid and like hydroxycarboxylic acids; etc.

[0020] Examples of usable alcohol components include ethylene glycol, diethylene glycol, triethylene glycol,

- 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, 1,10-decanediol, neopentyl glycol, spiroglycol, 1,10-decanediol, 1,4-cyclohexane dimethanol, 2,2,4-trimethylpentane-1,3-diol, trimethylolethane,
- trimethylolpropane, glycerin, pentaerythritol, etc.

 [0021] The polyester resin for use in the present invention can be produced, for example, by a conventional process for producing polyester resins for powder coating compositions, using, as raw materials, an acid component

25 and alcohol component as mentioned above. For example, a

polyester resin can be produced by a process in which such raw materials are suitably combined and subjected to an esterification or ester exchange reaction by a standard method at 200 to 280°C, and after reducing the pressure to 5 hPa or lower, a polycondensation reaction can be performed at 230 to 290°C in the presence of a catalyst to obtain a resin with a high degree of polymerization, which is then subjected a depolymerization reaction with an alcohol component. The polyester resin preferably has 10 a softening temperature of 50 to 150°C. When the softening temperature is lower than 50°C, the resulting powder coating composition is susceptible to blocking and difficult to handle. When the softening temperature is higher than 150°C, the smoothness and continuity of the 15 coating film are impaired during the film-forming step after application of the coating composition, eliminating the effect of intercepting hazardous substances leaching out from the undercoat layer.

[0022] It is preferable to use a blocked isocyanate resin as mentioned above for crosslinking and curing the polyester resin. In such a case, the ratio of hydroxy groups in the polyester resin to latent isocyanate groups in the blocked isocyanate resin which contribute to the reaction, i.e., NCO/OH ratio, is preferably from 0.6 to 1.2, and more preferably from 0.8 to 1.0.

coating layer or polyester resin coating layer on the inner surface of a water pipe of the present invention can be formed using a powder coating composition, aqueous dispersion powder coating composition, non-solvent coating composition, electrodeposition coating composition or the like. It is preferable to use a powder coating composition from the viewpoint of application workability and film performance. Epoxy resin powder coating compositions, acrylic resin powder coating compositions and polyester resin powder coating compositions that are

compositions, acrylic resin powder coating compositions and polyester resin powder coating compositions that are preferably usable in the present invention can be prepared by conventional production processes for powder coating compositions.

[0024] In the step of mixing raw materials used as film components and thereby forming a blend, a solid resin material as a main ingredient, a coloring pigment, curing agent, additives, and optionally a small amount of liquid material are mixed as homogeneously as possible. For this purpose, conventional apparatuses for mixing raw materials are usable, such as flush mixers, screw mixers, conical blenders, V mixers, tumbling mixers, jet mixers, kneaders, ribbon mixers, etc.

[0025] Apparatuses usable for melting and kneading include roll mills, screw kneaders, mullers, kneaders, etc. It is

preferable to use an apparatus that makes it possible for the molten and kneaded product to be promptly discharged from the apparatus and cooled. In particular, when the resin particles of the powder coating composition contain a curing agent, the resin component, curing agent and other components are homogeneously mixed in the melting and kneading step. At that time, the blend is heated to the softening temperature of the resin component or higher, and thus a prolonged residence time during kneading causes part of the resin component to react with the curing agent. 10 When such partially reacted resin particles are used for coating, it is likely that the resulting coating film is not smoothly continuous or has defects such as lacking gloss. Accordingly, it is preferable to use an apparatus in which the feed is supplied from one side and the molten 15 and kneaded product is continuously discharged from another side. The molten and kneaded product is cooled and then pulverized with a grinding and classifying machine to obtain a powder with a predetermined particle size distribution. The surface of this powder is post-20 treated with a fluidizing agent or the like to obtain a powder coating composition.

[0026] In the present invention, the inner surface of the water pipe can be coated by causing a powder coating

25 composition to be carried by an air flow from one end of a

water pipe; by inserting a powder coating gun inside the water pipe and coating the inner surface while withdrawing the gun; or other methods. Also, the devices for applying the undercoat and overcoat layers can be inserted in the water pipe concurrently to apply undercoat and overcoat layers substantially simultaneously with only a short interval, thereby forming coating films.

[0027] Coating methods usable in the present invention include a method in which, after pretreatment, an

undercoat layer powder coating composition is applied to a water pipe that has been preheated to a temperature not lower than the resin softening temperature in a preheating oven or induction heating apparatus, and then an overcoat layer powder coating composition is applied to the lower

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layer powder coating composition in a melted state while being formed into a film, followed by curing the two layers simultaneously to form films; and a method in which an undercoat layer powder coating composition is applied to a water pipe at room temperature and heated to form a completely cured film of the undercoat layer powder coating composition, and then an overcoat layer powder coating composition is applied by the same procedure to form a film.

[0028] When the water pipe is preheated to a temperature not lower than the resin softening temperature, it is

before the temperature drops, an overcoat layer powder coating composition is applied so that the two layers are cured simultaneously by the residual heat; and (iv) a method in which, in process (iii), the two layers are further heated for curing during the simultaneous curing.

[0030] The method for producing an inner surface-coated water pipe may further comprise applying a clear coating composition after the application of the overcoat layer coating composition, i.e., the acrylic resin powder coating composition or polyester resin powder coating composition.

[0031]

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[Examples] The present invention is described below in further detail with reference to Production Examples and Examples. In these Production Examples and Examples, parts are expressed on a weight basis.

<Production of an undercoat layer powder coating
composition> A polyester resin (32 parts) having a
softening temperature of 120°C and an acid value of 45, a
bisphenol A-type epoxy resin (32 parts) having an epoxy
equivalent of 910, a titanium pigment (20 parts), talc (10
parts), a surface modifier (5 parts), and a curing
accelerator (1 part) were mixed using a screw mixer and
rendered homogeneous using a flash mixer.

[0032] A twin-screw kneader was used as a melt-kneading machine with the heating temperature being set at 115°C. A twin-roller cooler that can be used for cool-rolling was provided on top of the melt-kneading machine, and a hammer 5 top of the cooler. crusher was provided on The homogenously mixed material was supplied from a feeder of the twin-screw kneader. The mixture was homogenized after about 20 seconds of residence and knead-dispersion. This homogenized substance was dropped as a viscous liquid of about 120°C from the top of the twin-screw kneader to 10 reduction rolls of the twin-roller cooler, rolled, cooled in about 10 seconds to almost room temperature, and the thus-obtained platy resin particulate material was preliminarily crushed to coarse powder resin particles 15 having a diameter of about 0.5 mm using a hammer crusher. preliminarily crushed coarse [0033] The powder continuously pulverized using a turbo grinder, and classified using a 120 mesh classifier. Colloidal silica (0.8 parts) and the resin particles which had been classified were homogeneously mixed and subjected to a 20 post-treatment, obtaining an undercoat layer powder coating composition.

[0034] <Production of overcoat layer powder coating composition 1> In a dropping vessel were homogeneously dissolved 60 parts of methyl methacrylate, 6 parts of

butyl acrylate, 33 parts of glycidyl methacrylate, and 1 part of azoisobutyronitrile. Xylol (100 parts) was placed in a reaction vessel and heated to 120°C. While stirring this reaction vessel, the solution in the dropping vessel was added to the reaction vessel dropwise over one hour and the resultant was left for two hours. Thereafter, 0.3 parts of azoisobutyronitrile was further added thereto, the resultant was left at 150°C for about 4 hours to proceed a polymerization reaction, obtaining a resin solution.

[0035] This resin solution was treated with a thin-film decompression dryer to remove the solvent, obtaining a solid acrylic resin. The softening temperature of this acrylic resin was about 55°C and molecular weight thereof 7000. 15 about This acrylic resin was (77 parts), dodecanedicarboxylic acid (19 parts), a surface modifier (1 part) and a fluidizing agent (3 parts) were mixed. The mixture was melt-kneaded, pulverized, classified, subjected to a post-treatment in the same manner as the above-described production of an undercoat layer powder 20 coating composition, obtaining overcoat layer powder coating composition 1.

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[0036] <Production of overcoat layer powder coating composition 2> Fifty-six parts of a polyester resin (manufactured by Dainippon Ink and Chemicals, Incorporated,

product name: Finedic M8023, softening temperature of 110°C, hydroxyl value of 40), 11 parts of a block isocyanate resin (manufactured by Daicelhuls, Ltd., product number: IPDI-B1530), 1 part of a surface modifier, 2 parts of a fluidizing agent, 29 parts of titanium oxide, and 1 part of carbon black were mixed. The mixture was melt-kneaded, pulverized, classified, and subjected to a post-treatment in the same manner as the above-described production of an undercoat layer powder coating composition, obtaining overcoat layer powder coating composition 2.

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[0037] <Production of overcoat layer powder coating composition 3> The acrylic resin obtained in the above-described production of overcoat layer powder coating composition 1 (77 parts), dodecanedicarboxylic acid (19 parts), a surface modifier (1 part), and a fluidizing agent (3 parts) were mixed, melt-kneaded, pulverized and classified, obtaining resin particles for acrylic resin clear powder coating composition. To 93 parts of these resin particles was dry-blended 6 parts of an aluminum pigment (particle diameter of 30 µm, aspect ratio of about 10), 1 part of a silica fine powder was added thereto, and the mixture was subjected to a post-treatment, obtaining overcoat layer powder coating composition 3.

25 [0038] <Example 1> A cast iron tube was preliminarily

heated to evaporate and remove oil, etc. When the temperature of this cast iron tube had fallen to 200°C to 220°C, an undercoat layer powder coating composition was supplied from an air flow vessel to an electrostatic powder coating gun, and coating was conducted in such a manner that the film thickness became about 700 µm while withdrawing the coating gun from the cast iron tube.

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[0039]

Sixty seconds after the application of the undercoat layer powder coating composition, overcoat layer powder coating composition 1 was applied using another electrostatic powder coating gun in such a manner that the thickness of overcoat layer powder coating composition 1 was about 100 μm , the resultant was left for 3 minutes, and cooled using water, obtaining a water pipe with a coated inside. When a cross section of this pipe was observed using a microscope, the layer of the undercoat layer powder coating composition and the clear layer of the overcoat layer powder coating composition formed two separate layers that were not intermixed to each other. Furthermore, when the surface of the coating film was

analyzed using FTIR, neither absorption peaks due to the formula attributable to bisphenol A structural nor absorption peaks attributable to the structural formula of the epoxy resin both contained in the undercoat layer powder coating composition were observed. Water was

placed in the coated cast iron tube and left at 40°C for 1000 hours. A microanalysis of the water was conducted and bisphenol A was not detected.

[0040] <Example 2> An electric-resistance-welded pipe was subjected to emulsion degreasing, heated and dried. Coating gun equipment having gun necks longer than the pipe was used. A gun for an undercoat layer powder coating composition and a gun for an overcoat layer powder coating composition were provided on the head of the coating gun equipment 50 cm apart, and the guns were 10 connected to their respective coating composition feeders. [0041] The coating gun equipment was prepared in such a manner that an undercoat layer powder coating composition supplied to a gun on the withdrawal-direction and overcoat layer powder coating composition 2 was supplied 15 to a gun on the back side, and cold water was circulated through the supporting part and the coating guns. electric-resistance-welded pipe was heated in a preheating oven at 250°C, transferred into a coating equipment, and 20 rotated at 200 r.p.m. The coating guns were inserted into the water pipe in such a manner that the top ends of guns emerged from the other end of the pipe, and the coating compositions were immediately sprayed while withdrawing the coating guns at 20 m/min. The undercoat layer and the overcoat layer were coated with a timing difference of 25

about 1.5 seconds. The coated layers were left for 3 minutes and cooled with water, obtaining a water pipe. When a cross section of this pipe was observed using a microscope, the layer of the undercoat layer powder coating composition and the layer of the overcoat layer powder coating composition formed two separate layers.

[0042] As in Example 1, the surface of the coating film was analyzed using FTIR, and neither absorption peaks due to the structural formula attributable to bisphenol A nor 10 absorption peaks attributable to the structural formula of the epoxy resin both contained in the undercoat layer powder coating composition were observed. Water was placed in the pipe and microanalysis of the water was conducted in the same manner in Example as and bisphenol A was not detected. 15

same manner as in Example 1 except that overcoat layer powder coating composition 3 was used instead of overcoat layer powder coating composition 1, and then evaluated. The results were that bisphenol A was not detected on the surface of the coating film nor in the water in the pipe. Furthermore, the water absorptivity and water permeability of a coating film formed solely of overcoat layer powder coating composition 1, and the water absorptivity and water permeability of the coating film formed solely of

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[0043] <Example 3> Coating process was conducted in the

overcoat layer powder coating composition 3 containing flaky pigments were measured. Both the two coating films had a water absorptivity of 0.7% so that no great difference was observed. However, the water permeability of the coating film formed of overcoat layer powder coating composition 3 was half that of the coating film formed of overcoat layer powder coating composition 1, and therefore a significant advantage was observed.

[0044] <Comparative Example 1> A water pipe was prepared following the same method of Example 1 except that an 10 undercoat layer powder coating composition was coated in such a manner that the film thickness was about 800 µm and no overcoat layer powder coating composition was applied. The surface of the coating film was analyzed using FTIR, 15 absorption peaks due to the structural formula and bisphenol A attributable to and absorption attributable to the structural formula of the epoxy resin both contained in the undercoat layer powder coating composition were observed.

20 [0045]

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[Effect of the Invention] As described above, the water pipe with a coated inner surface of the present invention can be produced without drastically changing the steps, time, costs, etc., of prior art coating techniques. The present invention can add corrosion resistance to a water

pipe, and prevent hazardous substances from entering tap water.